

Original Research Article

Kinetic of Corrosion for V_2AlC and Cr_2AlC at pH=11.7

Abstract

Corrosion behavior of MAX phase materials have been investigated in 0.01N $Ca(OH)_2$ at pH=11.7 using Potentiostat to estimate corrosion parameters. The results show that V_2AlC material has more noble potential and lower current density than Cr_2AlC over temperatures include 303, 313, 323 and 333K. Polarization resistance which calculated according to Stern-Geary equation confirms the most resistance for V_2AlC in experimental conditions. Thermodynamic functions refer to that the change in free energy more negative for Cr_2AlC than V_2AlC , this means that V_2AlC has less ability to corrosion. The negative value of ΔS for V_2AlC confirms the later result. Also activation energy E_a for V_2AlC more than for Cr_2AlC .

Keywords: MAX phase material, corrosion in $Ca(OH)_2$, kinetic of corrosion.

Introduction

Many authors interested by fabrication of MAX phase materials and investigated on their properties such as physical and mechanical properties including elasticity, electrical and thermal conductivity, hardness and electrical resistance [1-16]. These materials characterize by regular lattice structure, i.e. lower defects in crystal structure. There are few studies concerned with corrosion behavior of MAX phase material as reproducible industrial materials. Many authors highlighted corrosion of MAX phase materials at high temperatures (oxidation). While there are very little studies focused the corrosion at normal temperatures. V.D. Jovic et al. studied the corrosion behavior of select MAX phases in 1M of NaOH, HCl and H_2SO_4 [17]. Also, Dong et al. studied the corrosion of Cr_2AlC compounds [18]. Rana et al. studied the corrosion behavior of V_2AlC and Cr_2AlC in 0.01N NaCl solution [19].

The present work involves study the corrosion behavior of two MAX phase materials in 0.01 $Ca(OH)_2$ at four different temperatures by potentiostat to estimate the corrosion resistance of these materials.

Experimental Procedure

MAX phase materials were fabricated using powder metallurgy by weighting certain weight of V, Cr, C, and Al powders (99% pure), mixing using ball milled, cold pressing and sintering at 1100-1350°C for 6 hrs.

Characterization of fabricated materials was achieved using X-ray diffraction and scanning electron microscope. Corrosion behavior of these materials was estimated by potentiostat type WINKING M Lab 200 at 5 mV.sec⁻¹ to obtain corrosion parameters such as corrosion potential, corrosion current density and Tafel slopes. All experiments were performed at four temperatures using jacket cell at four temperatures 30, 40, 50 and 60°C corresponding to 303, 313, 323 and 333K.

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Results and Discussion

Figure (1) shows the XRD of prepared materials which confirms the presence of MAX phases. Figs. (2) and (3) show the polarization curves of V_2AlC and Cr_2AlC respectively in calcium hydroxide at pH = 11.7 at four different temperatures, these curves show the cathodic and anodic regions represented by reduction of oxygen at cathodic sites and oxidation of metals at anodic sites followed by form protective films to protect materials in corrosive environment. The data of corrosion were measured using Tafel extrapolation method as listed in Table (1).

These data indicate that V_2AlC has more noble corrosion potentials than Cr_2AlC , and lower corrosion current densities which give indication about the corrosion rate. The higher corrosion resistance of V_2AlC due to the protective film of vanadium oxide on material surface. Cathodic Tafel slopes lower than anodic once, this means that the change in potential with current density was lower at cathodic sites than anodic once.

The data of polarization resistance R_p which calculated according to Stern-Geary equation [20], indicate that the resistance of V_2AlC more than for Cr_2AlC .

$$R_p = \left(\frac{dE}{di} \right)_{i=0} = \frac{b_a b_c}{2.303(b_a + b_c) i_{corr}}$$

where b_a and b_c are anodic and cathodic Tafel slopes respectively.

The free-energy change accompanying an electrochemical reaction can be calculated by the following equation[21]:

$$\Delta G = -nFE$$

where ΔG is the free-energy change, n is the number of electrons involved in the reaction, F is the Faraday constant, and E equals the cell potential ($E = E_{corr}$).

At constant temperature, the change in free energy more negative for Cr_2AlC than V_2AlC , this means that V_2AlC has less ability to corrosion.

From the value of ΔG at several temperatures, the change in the entropy (ΔS) of corrosion process could be derived according to the well-known thermodynamic relation:

$$\Delta S = - \frac{d(\Delta G)}{dT}$$

Values of ΔG are usually plotted against temperature (T); thus at any temperature the value of $-d(\Delta G)/dT = \Delta S$ which corresponds to the slope of the ($-\Delta G$) versus (T) plot at that temperature, as shown in Fig. (2). The change in free energy, ΔG , is related to ΔH , the change in the enthalpy, and ΔS , the change in entropy of the corrosion reaction at a constant temperature, T , by the equation [22]:

$$\Delta G = \Delta H - T\Delta S$$

The change in entropy was negative for V_2AlC , while positive value for Cr_2AlC , this means that the corrosion of V_2AlC gave stable corrosion products such as protective layer of metal oxide with less disorder than reactant. The positive values of ΔH refer to endothermic process of corrosion for MAX phase material.

The rate (r) of corrosion in a given environment is directly proportional with its corrosion current density (i_{corr}) in accordance with the relation [23]:

$$r = 0.13(e/\rho) i_{corr}$$

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here (e) is the equivalent weight of the metal and (ρ) is its density. For the increasing values of (i_{corr}) with a temperature follow Arrhenius equation, it is reasonable as:

$$i_{\text{corr}} = A \exp(-E_a / RT)$$

where A and E_a are the pre-exponential factor and energy of activation of the corrosion process respectively. Values of E_a were derived from the slopes of the ($\log i_{\text{corr}}$) versus ($1/T$) linear plots as in Fig. (3). The values of activation energy and $\log A$ for V_2AlC more than for Cr_2AlC , this result confirms more corrosion resistance of V_2AlC than Cr_2AlC .

Conclusion

Corrosion behavior of V_2AlC and Cr_2AlC materials have been investigated in 0.01N Ca(OH)_2 through the calculation of polarization resistance which indicate that V_2AlC more resistance than Cr_2AlC , also the corrosion process of V_2AlC less spontaneous than for Cr_2AlC through the change in free energy value. The negative value of ΔS for V_2AlC confirms the later result. Also activation energy E_a for V_2AlC was more than for Cr_2AlC .

References

- 1- Y. C. Zhou, X. H. Wang, Z. M. Sun and S. Q. Chen, "Electronic and structural properties of the layered ternary carbide Ti_3AlC_2 ", *J. Mater. Chem.*, 2001, 11, 2335–2339.
- 2- X.H. Wang and Y.C. Zhou, "Intermediate-temperature oxidation behavior of Ti_2AlC in air", *J. Mater. Res.*, Vol. 17, No. 11, Nov 2002
- 3- X.H. Wang, Y.C. Zhou, "Microstructure and properties of Ti_3AlC_2 prepared by the solid-liquid reaction synthesis and simultaneous in-situ hot pressing process", *Acta Materialia*, 50 (2002) 3141–3149
- 4- Zhimei Sun, Rajeev Ahuja and Sa Li, and Jochen M. Schneider, "Structure and bulk modulus of M_2AlC ($\text{M}=\text{Ti}$, V, and Cr)", *Appl. Phys. Lett.*, Vol. 83, No. 5, 4 August 2003.
- 5- Jochen M. Schneider, Zhimei Sun, Raphael Mertens, Fatih Uestela, and Rajeev Ahuja, "Ab initio calculations and experimental determination of the structure of Cr_2AlC ", *Solid State Communications* 130 (2004) 445–449.
- 6- J. D. Hettinger, S. E. Lofland, P. Finke, T. Meehan, J. Palma, K. Harrell, S. Gupta, A. Ganguly, T. El-Raghy, and M. W. Barsoum, "Electrical transport, thermal transport, and elastic properties of M_2AlC ($\text{M}=\text{Ti}$, Cr, Nb, and V)", *Physical Review B* 72, 115-120, 2005.
- 7- Yuri Khoptiar, Irena Gotman, and Elazar Y. Gutmanas, "Pressure-Assisted Combustion Synthesis of Dense Layered Ti_3AlC_2 and its Mechanical Properties", *J. Am. Ceram. Soc.*, 88 [1], 28–33 (2005).
- 8- Zhimei Sun, Denis Music, Rajeev Ahuja and Jochen M Schneider, "Ab initio study of M_2AlN ($\text{M}=\text{Ti}$, V, Cr)", *J. Phys.: Condens. Matter*, 17 (2005) L15–L19.
- 9- Wubian Tian, Peiling Wang, Guojun Zhang, Yanmei Kan, Yongxiang Li, and Dongsheng Yan, "Synthesis and thermal and electrical properties of bulk Cr_2AlC ", *Scripta Materialia*, 54 (2006) 841–846.
- 10- Wu-bian Tian, Pei-ling Wang, Guo-jun Zhang, Yan-mei Kan, and Yong-xiang Li, "Mechanical Properties of Cr_2AlC Ceramics", *J. Am. Ceram. Soc.*, 90 [5] 1663–1666 (2007).

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- 11- Denis Music, Jens Emmerlich and Jochen M Schneider, "Phase stability and elastic properties of $Ta_{n+1}AlC_n$ ($n = 1-3$) at high pressure and elevated temperature", *J. Phys.: Condens. Matter*, 19 (2007) 136207 (9pp)
- 12- Yanchun Zhou, Fanling Meng, and Jie Zhang, "New MAX-Phase Compounds in the V-Cr-Al-C System", *J. Am. Ceram. Soc.*, 91 [4] 1357-1360 (2008).
- 13- Wubian Tian, Peiling Wang, Yanmei Kan, and Guojun Zhang, "Oxidation behavior of Cr_2AlC ceramics at 1100 and 1250°C", *J Mater Sci.*, (2008) 43:2785-2791.
- 14- Wubian Tian, ZhengMing Sun, and Hitoshi Hashimoto, "Compressive deformation behavior of ternary compound Cr_2AlC ", *J Mater Sci*, (2009) 44:102-107.
- 15- W.B Zhou, B.C. Mei, and J.Q. Zhu, "On the synthesis and properties of bulk ternary Cr_2AlC ceramics", *Materials Science-Poland*, Vol. 27, No. 4/1, 2009.
- 16- Chang-Sam Kim, Sung Ik Hwang, Jung-Soo Ha, Seung-Min Kang and Deock-Soo Cheong, "Synthesis of a Cr_2AlC - Ti_2AlC ternary carbide", *Journal of Ceramic Processing Research*. Vol. 11, No. 1, pp. 82-85 (2010).
- 17- V.D. Jovic, B.M. Jovic, S. Gupta, T. El-Raghy and M.W. Barsom, "Corrosion behavior of select MAX phases in NaOH, HCl and H_2SO_4 ", *Corrosion Science*, Vol.48, pp.4274-4282 (2006).
- 18- Dong Bok Lee, Thuan Dinh Nguyen, and Sang Whan Park, "Corrosion of Cr_2AlC in Ar/1% SO_2 Gas Between 900 and 1200 °C", *Oxidation of Metals*, Vol.75, Issue 5-6, pp 313-323, June 2011.
- 19- Rana Afif Majed, Ahmed M. Al-Ghaban, Russul F. Faleh, "Corrosion Behavior of V_2AlC and Cr_2AlC MAX phase Materials in 0.01N NaCl", *Asian Journal of Engineering and Technology*, Vol.2, Issue 3, pp.244-254, (2014).
- 20- Rana A. Majed, Hanaa Al-Kaisy, and Hind B. Al-Atrakchy, "Effect of Chloride Ions on the Corrosion Behavior of Al-Zn Alloy in NaOH Solution at Four Different Temperatures", *Al-Khwarizmi Engineering Journal*, Vol.4, No.4, PP.26-36 (2008).
- 21- L. L. Sherir, "Corrosion", *Metal/Environment Reactions*, second ed. vol.1, pp. 4:12, (1976).
- 22- Naema A. Hikmat, Ahlam M. Farhan and Rana A. Majed, "Effect of Deaeration on the Corrosion of Pure Aluminum and Its Three alloys in NaOH solution at pH=11", *Eng. & Tech. Journal*, vol.27, No.8, pp. 1532-1543 (2009).
- 23- Rana A. Majed, "Galvanic Corrosion of Dental Alloys and Amalgam in Artificial Saliva Containing Citric Acid", *Eng. & Tech. Journal*, vol.31, No.12, pp. 2299-2310 (2013).

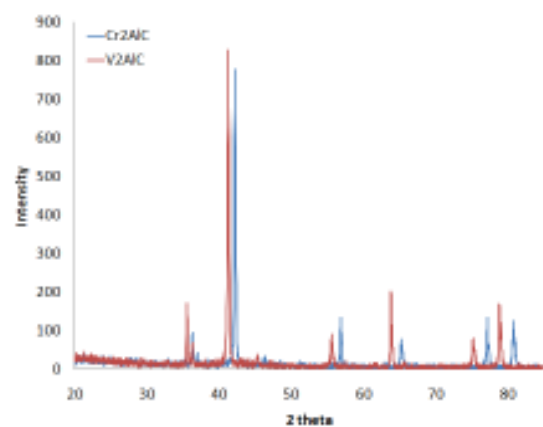


Fig. 1: XRD of prepared MAX phase materials.

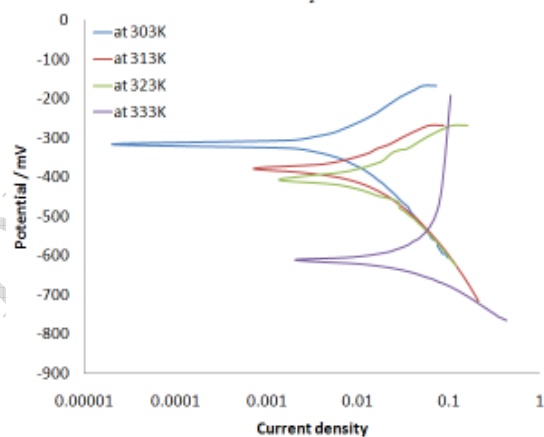


Fig. 2: Polarization curve of V_2AlC in $0.01N\ Ca(OH)_2$ at four temperatures.

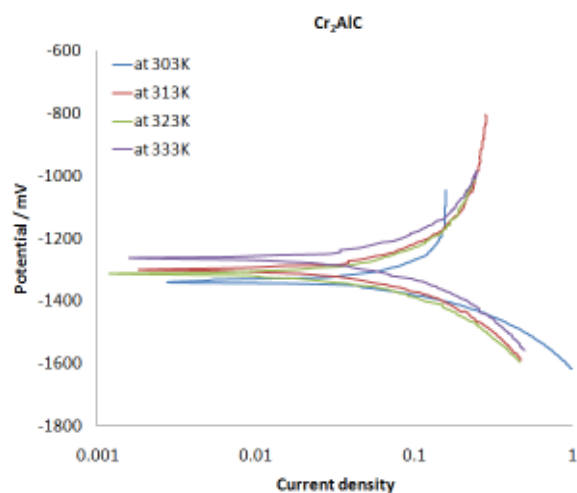


Fig. 3: Polarization curve of Cr_2AlC in 0.01N Ca(OH)_2 at four temperatures.

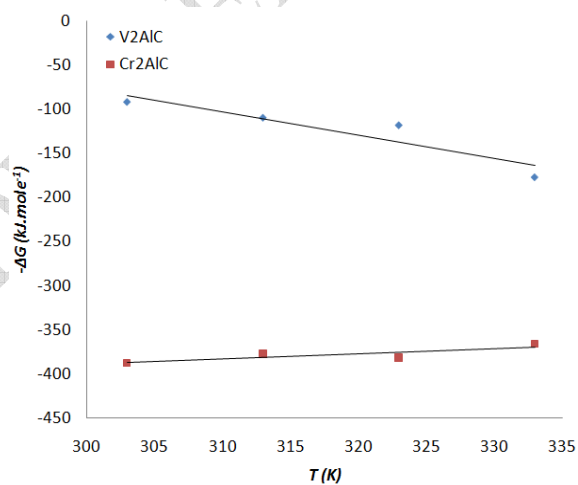


Fig. 4: The relationship between ΔG and T for MAX phase materials.

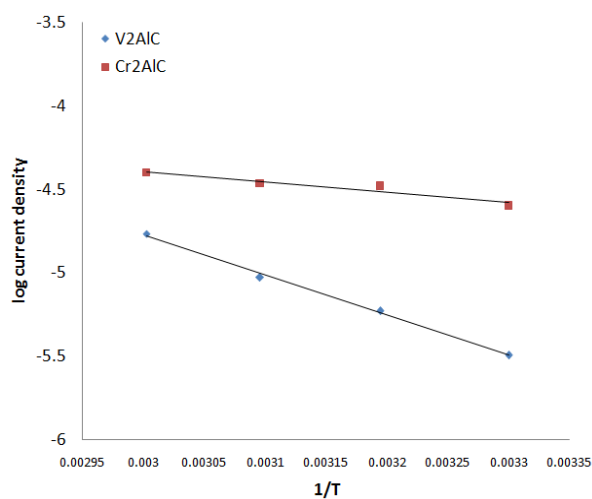


Fig. 5: Arrhenius plot for MAX phase materials.

Table (1): Corrosion parameters for V₂AlC and Cr₂AlC in 0.01N Ca(OH)₂ at four temperatures.

Material	Temp. K	E_{corr} mV	i_{corr} $\mu A.cm^{-2}$	$-b_c$ mV.dec ⁻¹	$+b_a$ mV.dec ⁻¹	$R_p \times 10^3$ $\Omega.cm^2$
V ₂ AlC	303	316.4	3.19	111.6	117.5	7.79
	313	378.4	5.88	110.0	128.8	4.38
	323	408.0	9.31	132.2	133.8	3.10
	333	612.6	17.00	82.8	124.5	1.27
Cr ₂ AlC	303	1338.8	32.31	85.7	128.7	0.69
	313	1304.5	32.95	139.1	176.8	1.03
	323	1319.5	34.29	147.6	199.2	1.07
	333	1266.2	39.56	167.6	214.9	1.03

Tables (2): The thermodynamic quantities for V₂AlC and Cr₂AlC in 0.01N Ca(OH)₂ at four temperatures.

Material	T (K)	-ΔG (kJ.mole ⁻¹)	ΔS (kJ.mol ⁻¹ .K ⁻¹)	ΔH (kJ.mole ⁻¹)
V ₂ AlC	303	91.60	-2.65819	0.29
	313	109.55		0.34
	323	118.12		0.36
	333	177.35		0.52
Cr ₂ AlC	303	387.58	0.587106	1.28
	313	377.65		1.21
	323	382.0		1.18
	333	366.56		1.10

Table (3): Values of activation energy (E_a), pre- exponential factors (A) for V₂AlC and Cr₂AlC in 0.01N Ca(OH)₂.

Material	E _a (kJ.mol ⁻¹)	Log A
V ₂ AlC	19.95	2.424
Cr ₂ AlC	12.80	0.337